THE MECHANISM OF CaO SULFATION IN BOILER LIMESTONE INJECTION

M. R. Stouffer, H. Yoon and F. P. Burke

CONSOLIDATION COAL COMPANY
Research & Development Department
4000 Brownsville Road
Library, PA 15129

ABSTRACT

Pilot and industrial-scale tests of boiler limestone injection (BLI) have demonstrated flue gas SO_2 reductions of around 50% at sorbent utilization efficiencies of 15-20%. The objective of the laboratory research program described in this paper was to improve BLI sorbent utilization through an understanding of the limestone calcination and CaO sulfation reaction mechanisms. This paper describes the laboratory sulfation studies. The laboratory work used a differential reactor operated at 700-1000°C and lab-produced calcines from limestones, dolomites, and hydrated limes, having particle sizes in a range applicable to BLI. The lab work determined the intrinsic sulfation reaction rate and rate-controlling steps over this temperature range. The intrinsic rate increased with the square of calcine surface area and was rate controlling only at temperatures below 800°C. At the higher temperatures more applicable to BLI, the sulfation rate was limited by pore diffusion of SO_2 and pore plugging by the sulfate product. Therefore, the reaction rate and the saturated sorbent efficiency depended strongly on particle size and calcine pore structure. The lab data indicate that an optimum calcine pore structure can be obtained by appropriately evaluating sorbents, controlling calcination conditions and incorporating alkali additives in the sorbent.

INTRODUCTION

Boiler limestone injection is a low capital cost SO_2 control technology, involving injection of pulverized limestone into the high-temperature (1000-1300°C) regions of a coal-fired furnace. Alternate calcium sorbents, such as hydrated lime and dolomite, can also be used. In 1984, Consolidation Coal Company (Consol) successfully demonstrated the technology using a 15 MW industrial boiler at Du Pont's Martinsville nylon plant (1). The target 50% SO_2 removal was achieved by injecting limestone at 2.5-2.75 Ca/S molar ratios, corresponding to 18-20% sorbent utilization efficiencies. Since then, Consol has conducted an extensive laboratory program studying the fundamental mechanisms involved in BLI. The objective has been to significantly improve the sorbent utilization by applying the fundamental information for process improvement.

SO_2 removal by BLI involves sequential calcination and sulfation reactions:

Calcination: $CaCO_3 \longrightarrow CaO + CO_2$

Sulfation: $CaO + SO_2 + 1/2\ O_2 \longrightarrow CaSO_4$
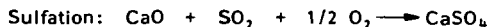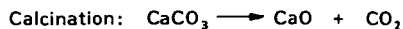
These reactions have been widely studied; however, much of the published work has been limited to low surface area (<5 m^2/g), large particle size (ca. 1 mm) calcines (CaO), applicable to fluidized bed combustion. The reactivities observed with these calcines are too low to provide significant SO_2 reduction in BLI (2). More recent studies at EPA (3-6) using very fine (ca. 1 micron) limestone particles have shown that very high surface area calcines (up to 80 m^2/g) could be produced by differential calcination in a dispersed-phase system. In these studies, the intrinsic sulfation activity of the very fine calcine particles was proportional to the square of the calcine BET surface area. This result suggests that production of a high

surface area calcine may be critical for BLI processes. However, the 1 micron limestone particle size used in the EPA studies is much smaller than practical sizes for BLI.

This paper reports a laboratory study of calcination and sulfation for sorbent samples having a range of particle sizes applicable to BLI. Detailed results of the calcination study were previously reported (7). In this work, calcines having up to 70 m^2/g surface area were produced under differential and dispersed conditions from pulverized limestone samples applicable to BLI. Calcine surface area depended on exposure time, temperature, CO_2 partial pressure, and stone properties. A kinetic model derived for the calcination reaction indicated that calcination occurs very rapidly (<0.1 sec) at BLI temperatures.

In the sulfation study, the intrinsic sulfation kinetics and rate-controlling steps were determined with lab-produced calcines from limestones, dolomites, and hydrated sorbents. In addition, the effect of alkali additive incorporation on limestone was studied as a means of enhancing sulfation performance of calcines. The temperature range of 700-1000°C, limited by the experimental apparatus, was lower than the BLI temperature range of 1000-1300°C. However, the lab data provided valuable insight into BLI sulfur capture mechanisms and comparison of different sorbent performance.

EXPERIMENTAL

Test Sorbents

Twelve test sorbents were evaluated including eight different limestones, two dolomitic stones, a hydrated lime and a pressure-hydrated dolomite (Table 2). These sorbents varied widely in particle size as indicated by their specific surface mean diameters, and yielded calcines with widely varying BET surface areas (35-70 m^2/g). Most of the kinetic data were obtained for calcines produced from one stone, the Dravo Maysville -100 (#1). The other stones in Table 1 were tested for comparison.

Differential Reactor

A differential reactor (Figure 1) was used to calcine sorbent samples and to measure the sulfation performance of the calcines. This unit allowed control of reaction temperature to within ±3°C and sorbent/SO_2 contact time to within ±1 sec. To maintain differential sulfation conditions with respect to SO_2 partial pressure and temperature and to eliminate bulk mass transfer resistance, very small sorbent samples (down to 8 mg) well-dispersed in quartz wool and large flows (up to 70 scfh) of SO_2-containing sweep gas were used. Differential sulfation conditions were confirmed up to 900-950°C. Differential conditions were not possible above 950°C because of the extremely high sulfation rate. A few tests at 1000°C provided saturated sorbent utilization data, but no accurate rate data.

Test Procedures

Before sulfation, the sorbent was calcined in the differential reactor, under a purge flow of air at the same temperature as the subsequent sulfation. The calcination contact time was set to control the calcine surface area. For runs with low surface area calcines, the sorbent was calcined externally in a muffle furnace. After calcination was complete, the purge gas was switched immediately to an SO_2-containing gas containing 80% N_2, 15% CO_2, 5% O_2 and 750-3000 ppm SO_2. Immediately after a set reaction time between 5 and 600 sec, the SO_2-containing gas was shut off and the sorbent sample removed from the reactor. The conversion of CaO to $CaSO_4$ was determined by the Ca and S contents in the recovered sample

measured by atomic adsorption spectroscopy and combustion infrared detection, respectively.

Surface area and pore volume distributions of the calcine intermediates were measured separately by producing calcine samples under conditions duplicating those used prior to sulfation. Calcine surface areas were determined by N_2 adsorption at 77K (liquid N_2) and the one-point BET method. Pore distributions were determined from N_2 desorption isotherms (at 77K) following the methods detailed in References 8 and 9.

DISCUSSION OF RESULTS

Intrinsic Sulfation Kinetics

Intrinsic sulfation rate data measured for calcines from Dravo -100 mesh limestone were correlated by a kinetic model, originally proposed by Borgwardt (6). Based on the classical unreacted core model or grain model, this model relates fractional calcium conversion (x) to the SO_2 contact time (t, sec), absolute temperature (T, K), SO_2 partial pressure (P_{SO_2}, mmHg), and calcine specific surface area (A, m^2/g) as follows:

$$1 - 3 (1-x)^{2/3} + 2 (1-x) = k_d \cdot t \qquad (1)$$

$$k_d = K (A)^m (P_{SO_2})^n \exp (-E/RT) \qquad (2)$$

where the constants are

E = 37 kcal/mol, the activation energy
m = 2.0
n = 0.62
K = 50

The model equation is applicable to any calcine (CaO), since it includes a calcine property, the specific surface area, A. The intrinsic rate increased with the square of the surface area.

In the original development of this kinetic model, Borgwardt (6) used extremely small (95 wt % <2 micron, 30 wt % <1 micron) calcine particles, in order to eliminate pore diffusion limitation. Because of the much larger particle sizes used in the current study (13.4 micron specific surface mean diameter and 28.3 mass median diameter for the Dravo stone, #1), intrinsic rate data without pore diffusion limitation were measured only at low temperatures (≤800°C) and with low surface area calcines (<15 m^2/g). Figure 2 shows the good agreement of laboratory data at 800°C with the kinetic model predictions.

Pore Diffusion Limitation

With calcines produced from sorbent samples having particle sizes applicable to BLI (Table 1), pore diffusion was rate limiting at higher temperatures (>800°C) and with higher surface area calcines (>15 m^2/g). As a result, observed sulfation rates were significantly lower than the intrinsic rate predicted by the above model. As discussed below, pore diffusion limitation was evidenced by the observed reaction rate dependence on temperature, SO_2 partial pressure, particle size, and calcine surface area and pore structure.

Figure 3 shows that for higher surface area calcines, the apparent activation energy dropped from 37 kcal/mol to 15-20 kcal/mol at higher temperatures, indicative of transition to pore diffusion control. This agrees with the theoretical prediction that

$$E_{apparent} = \frac{E + E_{diffusion}}{2} \doteq E/2 \text{ under strong pore diffusion control.}$$

The onset of pore diffusion limitation for higher surface area calcines was around 800°C, based on the changes in slope in the Arrhenius plots. For a low surface area calcine (4 m^2/g), pore diffusion limitation was not evident up to 950°C, based on the activation energy.

The reaction order (n) in SO_2 partial pressure, measured at 900°C with a 55 m^2/g calcine, was 0.80 over 750-3000 ppm SO_2 concentrations, as compared with 0.62 according to the intrinsic kinetics. This change in the reaction order was also indicative of the pore diffusion control.

Because of the pore diffusion limitation, the initial sulfation rate observed at 900°C varied inversely with particle size (Figure 4). The different stone samples (#1-10) in Table 1 provided the variations in the particle size in the figure.

Under pore diffusion control, the effect of calcine surface area was diminished and high surface area calcines did not necessarily give high reactivity. This is because a calcine with very high surface area contains predominantly very fine pores which are more subject to pore diffusional resistance as well as pore mouth plugging, as discussed below.

Calcine Pore Plugging

Calcine pore mouth plugging by product $CaSO_4$ limited sulfation of highly porous calcines at higher temperatures. Limitation by pore plugging was evident in the lab tests from the exceptionally low apparent activation energies (<10 kcal/mol) observed with some very high surface area calcines and from the reduction in the saturated calcium utilization with increasing sulfation temperature for most of the calcines.

Porous calcines are subject to pore plugging by product sulfate because the molar volume of $CaSO_4$ (46.0 cm^3/mol) is considerably greater than that of CaO (16.5 cm^3/mol). If the mouth of a pore plugs before the interior undergoes reaction, the sorbent utilization is reduced. Further, pore mouth plugging by $CaSO_4$ can reduce the rate of sulfation by reducing available surface area and by increasing the pore diffusional resistance. Severe product pore mouth plugging is most likely when the rate of sulfation exceeds the rate of diffusion through the pores. Therefore, the degree of deactivation by pore plugging can be expected to increase with increasing temperature because the intrinsic sulfation rate increases more rapidly with temperature than the diffusion rate. Because of this temperature effect, pore plugging can reduce the apparent activation energy for sulfation. Deactivation by pore plugging can be expected to be most severe for smaller pores because the diffusion rate is slower and less $CaSO_4$ is required for complete pore blockage.

The degree of limitation of sulfation by pore plugging varied widely among calcines produced from different sorbents (Table 2). The apparent sulfation activation energies (based on initial reaction rates) among the different calcines ranged from negative values up to 22 kcal/mol. The activation energies below 15 kcal/mol indicate a rapid pore plugging at a higher temperature since the activation energies are lower than that under pore diffusion control. The wide variation in the activation energy among calcines indicates varying severity of pore plugging with these calcines. The saturated utilizations also varied widely among different calcines (17-80% at 900°C), as did the degree of temperature dependence of the saturated conversion.

The test data confirmed the more severe limitations by pore plugging for calcines with smaller pores. Figure 5 shows that a calcine from Genstar (#6) limestone had

significantly finer pores (mostly 3-10 nm) and less total pore volume than a calcine from the Dravo limestone (#1). The Dravo calcine had many pores in the 8-30 nm range. The apparent activation energy with the Genstar calcine was only 1.4 kcal/mol, significantly lower than the 15 kcal/mol observed for the Dravo calcine. Further, the Genstar calcine showed a more severe drop in final (saturation) calcium utilization with increasing temperature, from 36% to 27% to 18%, at 800°C, 900°C and 1000°C, respectively. The final utilizations with the Dravo calcine were 37%, 36% and 33% at these temperatures.

Performance of Different Stones/Sorbents

Limestones: Eight different limestones tested exhibited widely varying sulfation performance (Table 2). Saturation utilizations at 900°C varied from 17% to 50% and apparent activation energies varied from 1.4 to 22 kcal/mol over 800-950°C. These differences resulted from differences in both the stone particle size (Table 1) and the calcine intermediate pore structure. Calcine intermediate pore structure (surface area and pore size distribution) varied widely with limestone source. However, the specific properties of the original limestone which lead to a favorable calcine pore structure were not clearly identified.

Dolomitic Stones: Calcines from two dolomitic stones (Tables 1, 2) tested showed poor sulfation performance, presumably due to the presence of very small pores. Both showed negative apparent sulfation activation energies and low saturated calcium utilizations (22% at 900°C), indicative of premature pore plugging. Both calcines had very high surface areas (70 m²/g). Pore volume analysis of the calcine from the Hommel dolomite (#9) showed that it had over 85% of its pore volume in small pores, 2-10 nm in diameter.

Hydrated Sorbents: Calcines derived from a hydrated lime and a pressure-hydrated dolomitic lime showed better sulfation performance, in terms of both rate and saturation calcium utilization, than those derived from most limestones or dolomites. For the Dravo Longview hydrated lime (#11), saturated utilization was 55% at 800°C and dropped only to 53% at 900°C (Table 2). The apparent activation was 20 kcal/mol. Figure 6 clearly shows the superior sulfation performance of a calcine from a pressure hydrated dolomite (#12) to that from a dolomitic limestone (#9), the two calcines having roughly the same chemical composition. Saturated calcium utilizations were 80% and 22% for the pressure dolomitic hydrate and the dolomitic stone, respectively. Also, the saturated calcium utilization with the pressure hydrate did not drop at higher temperature. The excellent performance of the pressure hydrated dolomite again can be attributed to the formation of a very favorable calcine pore structure. Pore volume analysis showed that the calcine from the pressure hydrate had a broad pore size distribution (4-40 nm diameter) with about 60% of its total pore volume contributed by pores of 10 nm diameter and larger, as compared with the predominance of very small pores found in the calcined dolomite.

Sulfation Enhancement by Additive Promotion

Of several salts (Na_2CO_3, NaCl, $CaCl_2$, $FeCl_3$) tested, Na_2CO_3 was found to be the most effective in enhancing the desulfurization performance of limestone. Additives were incorporated in small amounts (0.25-5 wt %) in the limestone sample prior to calcination. The results indicate that the enhancement was primarily due to physical effects, increasing the pore size of the calcine to a range more favorable for pore diffusion. This agrees with the alkali additive effects on calcine porosity in FBC (10-13). The degree of enhancement increased with the Na_2CO_3 dosage up to 2 wt %.

For this additive study, additive effects were studied for two different limestones, the Dravo limestone (#1) and the Genstar limestone (#6) (Table 1). To produce an

additive promoted limestone sample, limestone was slurried in an aqueous additive solution. Water was then evaporated from the slurry. After preparation, the dry additive-enhanced limestone was charged in the differential reactor and calcined and sulfated in the usual manner.

Figure 7 shows that sodium carbonate promotion of the Dravo stone significantly increased pore size of the calcine intermediate. With no additive, a calcine produced at 900°C had pores mostly in the 6-20 nm diameter range. With 0.5 wt % and 2 wt % Na_2CO_3 in the stone, the 900°C calcines had pores mostly in the 6-40 nm and 10-70 nm ranges, respectively. Because of the increased pore size, calcine surface areas decreased. The BET surface areas for these calcines were 52, 21 and 10 m²/g, with Na_2CO_3 concentrations of 0, 0.5 and 2 wt %, respectively.

With the increase in calcine pore size with Na_2CO_3, the sulfation performance of the Dravo calcine was significantly enhanced (Figure 8). At 0.5 and 2 wt % additive dosages, saturated calcium utilizations at 900°C increased from 36% (with no additive) to 47% and 52%, respectively. Observed initial sulfation rates were also increased substantially. Similar enhancement was observed at 800°C and 1000°C. Further increase in the additive dosage above 2 wt % did not give additional sulfation enhancement. With 5 wt % Na_2CO_3 sulfation, performance of the Dravo calcine was not as good as with 2 wt % Na_2CO_3. The calcine with 5 wt % Na_2CO_3 had a low surface area (7 m²/g) and thus a lower intrinsic reaction rate. This result indicates that the pore size was increased excessively above an optimum level.

With Genstar limestone (#6), Na_2CO_3 showed similar positive effects. The saturated calcium utilization at 900°C was increased to 60% with 2 wt % Na_2CO_3, a substantial improvement over the 27% utilization with no additive. Initial reaction rate was likewise enhanced.

Other additives tested were not as effective as Na_2CO_3 in promoting sulfation. Sodium chloride (NaCl) showed some enhancing effect. The saturation conversion with calcined Dravo stone (#1) at 900°C increased from 36% to 42% at 2 wt % NaCl. Calcium chloride ($CaCl_2$) and ferric chloride ($FeCl_3$) showed no significant enhancement of sulfation performance.

<div align="center">CONCLUSIONS</div>

Sulfur capture by boiler limestone injection involves complex calcination and sulfation phenomena and is limited by both chemical and physical processes including intrinsic sulfation reaction, SO_2 pore diffusion in the calcine, and pore plugging by the product $CaSO_4$.

An intrinsic sulfation kinetic model, developed by Borgwardt of EPA, was experimentally confirmed. The intrinsic reaction rate increased with the square of calcine surface area and the 0.6 power of SO_2 partial pressure, and had an activation energy of 37 kcal/mol. The intrinsic reaction was rate limiting only at lower temperatures (≤800°C) and with lower surface area calcines (<15 m²/g).

Under conditions applicable to BLI, sulfation is limited by pore diffusion and by product pore mouth plugging. Observed sulfation rates at 900°C with high surface area calcines varied inversely with sorbent particle size because of the pore diffusion limitation. Because of the pore plugging effect, the capacity for sulfation was lower for calcines with finer pore structures. These results indicate that an optimum calcine pore structure (in terms of surface area and pore size) may exist for effective sulfation. The lab data indicate that the pore structure of a calcine depends on sorbent source and calcination conditions. Different limestones gave widely varying sulfation performances because they produced calcines having different pore structures. Hydrated sorbents gave significantly better sulfation performance

than limestones, because they yielded a more favorable calcine structure. These results indicate that sorbent selection for BLI may be very important.

Small amounts of sodium carbonate added to limestones prior to calcination yielded calcines with larger pores and thus significantly enhanced desulfurization performance.

REFERENCES

1. Fink, C. E., Harding, N. S., Koch, B. J., McCoy, D. C., Statnick, R. M. and Hassell, T. J., "Demonstration of Boiler Limestone Injection in an Industrial Boiler", 1st Joint Symposium on Dry SO_2 and Simultaneous SO_2/NOx Control Technologies, San Diego, California, November 13-16, 1984.

2. Borgwardt, R. H., "Kinetics of the Reaction of SO_2 with Calcined Limestone", Environmental Science and Technology 4, 59 (1970).

3. Borgwardt, R. H., Bruce, K. R. and Blake, J., "EPA Experimental Studies of the Mechanisms of Sulfur Capture by Limestone", Proceedings: 1st Joint Symposium on Dry SO_2 and Simultaneous SO_2/NOx Control Technologies, San Diego, California, November 13-16, 1984.

4. Borgwardt, R. H., "Calcination Kinetics and Surface Area of Dispersed Limestone Particles, "AIChE Journal, 31, 103 (1985).

5. Borgwardt, R. H., Roach, N. F. and Bruce, K. R., "Method for Variation of Grain Size in Studies of Gas-Solid Reactions Involving CaO", Ind. Eng. Chem. Fund., 25 (1), 1986.

6. Borgwardt, R. H. and Bruce, K. R., "Effect of Specific Surface Area on the Reactivity of CaO with SO_2", AIChE Journal, 32, 2 (1986).

7. Stouffer, M. R. and Yoon, H., "Laboratory Calcination and Sulfation Studies for Boiler Limestone Injection", presented at 6th Workshop on Coal Liquid and Alternate Fuels Technology, Halifax, Nova Scotia, September 1986.

8. Barrett, E. P., et al., "Determination of Pore Volume and Area Distributions in Porous Substances, I. Computations from Nitrogen Isotherms", Journal of American Chemical Society, 73, 3155, 1951.

9. Pierce, C., "Computation of Pore Sizes from Physical Adsorption Data", Journal of Physical Chemistry, 57, 147, 1953.

10. Shearer, J. A., Lenc, J. F., Johnson, I. and Turner, C. B., "The Effect of Sodium Carbonate Additive on the Reaction of SO_2/O_2 Mixtures with Carbonate Rocks", Argonne National Laboratory, Report ANL/CEN/FE-79-11, July 1979

11. Shearer, J. A., "The Effect of $CaCl_2$ Additive on the Reaction of SO_2/O_2 Mixtures with Carbonate Rocks", Argonne National Laboratory, Report ANL/CEN/FE-79-7, 1979.

12. Gasner, L. L., "The Addition of Salt to Fluidized Bed Combustors", Proc. Fifth Intl. Symposium on Salt - No. Ohio Geological Society, 439-445.

13. Shearer, J. A., Johnson, I. and Turner, C. B., "The Effects of Sodium Chloride on Limestone Calcination and Sulfation in Fluidized-Bed Combustion, Journal of Environmental Science and Technology.

TABLE 1

TEST SORBENTS

No.	Sorbent	Elemental Analysis CaO, wt %	MgO, wt %	Avg Particle Diameter, (a) micron Mass Median	Specific Surface Mean(b)	BET Surface Area of Raw Stone, m²/g	Maximum BET Surface Area of Calcine, m²/g
1	Dravo Maysville Limestone, -100 mesh	50.82	2.74	28.3	13.4	1.4	55
2	Dravo Maysville Limestone, -325 mesh	51.86	2.81	7.2	8.5	6.3	35
3	Pfizer Marble White 200 Limestone	54.79	0.36	23.1	14.6	0.7	60
4	Warner Bell Mine Limestone	54.71	0.58	25.9	15.8	1.8	45
5	Mississippi R-1 Limestone	55.20	0.30	300.0	112.0	0.9	70
6	Genstar Apex Limestone	56.53	0.46	28.3	16.1	1.0	60
7	Utah Marblehead Limestone	56.55	0.29	48.0	27.0	0.9	65
8	Baker Reagent $CaCO_3$	56.54	0.01	13.2	11.2	0.5	55
9	Hommel #1974 FF Dolomite	32.00	20.11	32.9	22.0	0.8	70
10	Warner Dolomite	28.90	21.96	98.2	55.8	0.3	70
11	Dravo Longview Hydrated Lime	72.01	2.44	12.0	12.0	21.1	40
12	Pressure Hydrated Dolomite	41.70	30.38	39.2	24.9	23.3	45

(a) Particle size determined by wet screening in CH_3OH and by Coulter Counter.

(b) Specific surface mean, $D_p = \dfrac{\Sigma\ Yi}{\Sigma\ YiDi}$

where Yi = weight fraction of size cut, Di = Average diameter of size cut.

TABLE 2

SULFATION PERFORMANCE OF HIGH SURFACE AREA CALCINES FROM TWELVE TEST SORBENTS

No.	Sorbent	D_p micron (a)	Calcine Surface Area, m²/g	$E_{apparent}$ (b)	Saturation Ca Conversion,% 800°C	900°C	1000°C (c)
1	Dravo Maysville Limestone, -100 mesh	24.5	55	15	39	36	33
2	Dravo Maysville Limestone, -325 mesh	8.5	35	15	50	50	36
3	Pfizer Marble White 200 Limestone	14.6	60	4.1	23	21	--
4	Warner, Bell Mine Limestone	15.8	45	15	37	33	23
5	Mississippi R-1 Limestone	112.0	70	4.1	20	17	9
6	Genstar Apex Limestone	16.1	60	1.4	36	27	18
7	Utah Marblehead Limestone	27.0	65	15	31	20	11
8	Baker Precipitated $CaCO_3$	11.2	55	22	45	36	--
9	Hommel #1974 Dolomite	22.0	70	Negative	32	22	--
10	Warner Dolomite	55.8	70	Negative	30	22	--
11	Dravo Longview Hydrated Lime	12.0	40	20	55	53	--
12	Pressure Hydrated Dolomite	24.9	45	21	80	80	--

(a) Specific surface mean particle diameter, as defined in Table 1.
(b) Apparent sulfation activation energy over 800-950°C.
(c) Runs at 1000°C deviated from differential conditions.
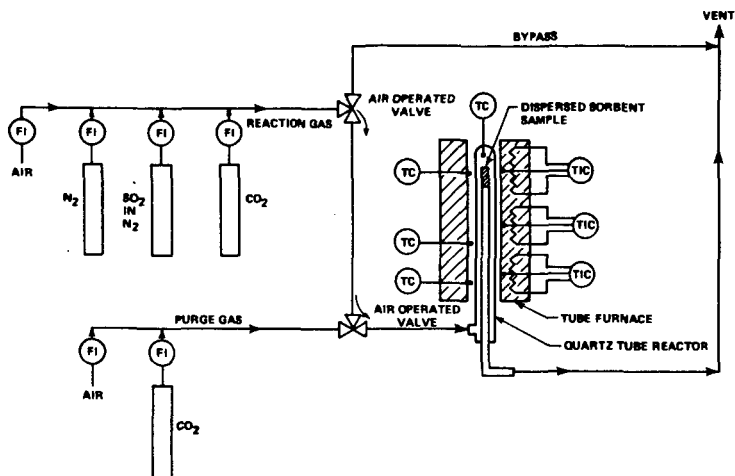
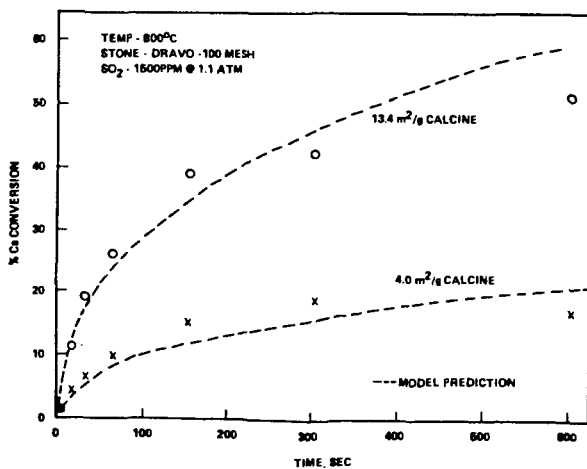Figure 1.   Schematic of Differential Reactor Unit.

Figure 2.   Comparison of Sulfation Rate Data with Intrinsic
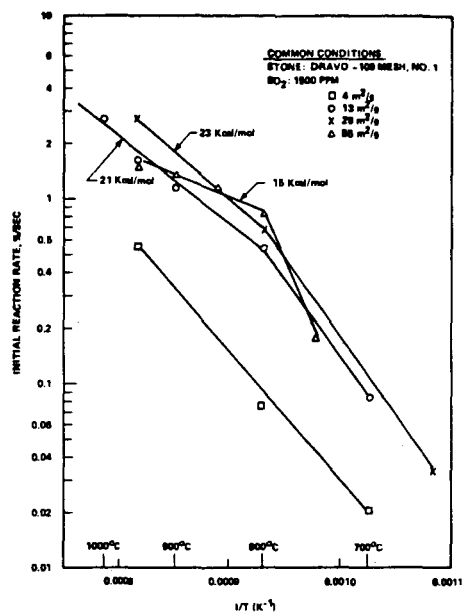Sulfation Kinetic Model.

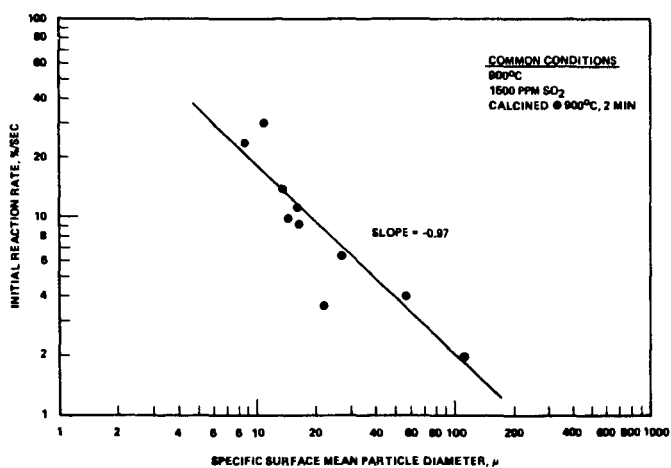Figure 3.   Initial Sulfation Rate vs Temperature.

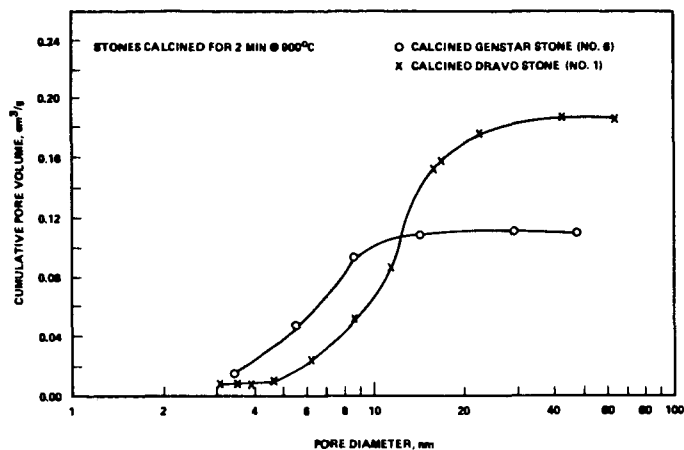Figure 4.   Effect of Stone Particle Size on Sulfation Rate.

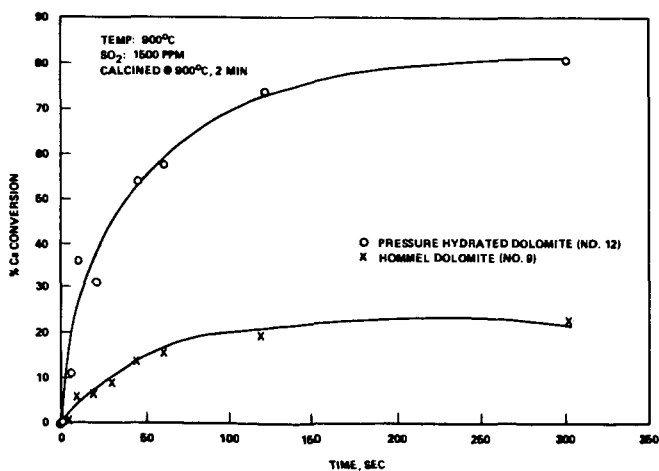Figure 5.   Cumulative Pore Volume Distribution for Two Calcined Limestones.

Figure 6.   Performance Comparison of Pressure Hydrated Lime
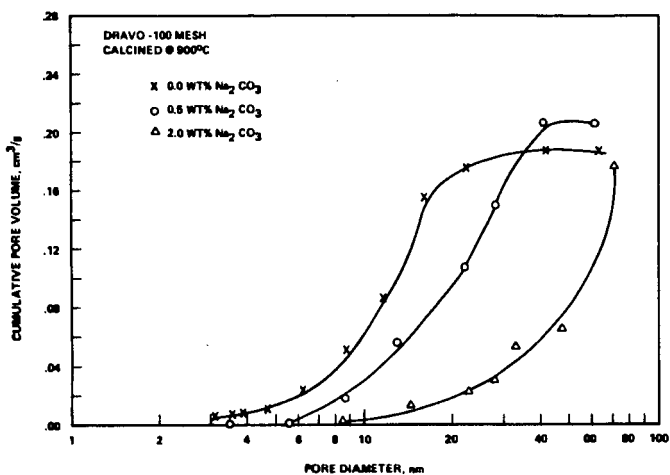and Dolomitic Stone.

Figure 7. Effect of Na$_2$CO$_3$ Additive on Calcine Pore Distribution.
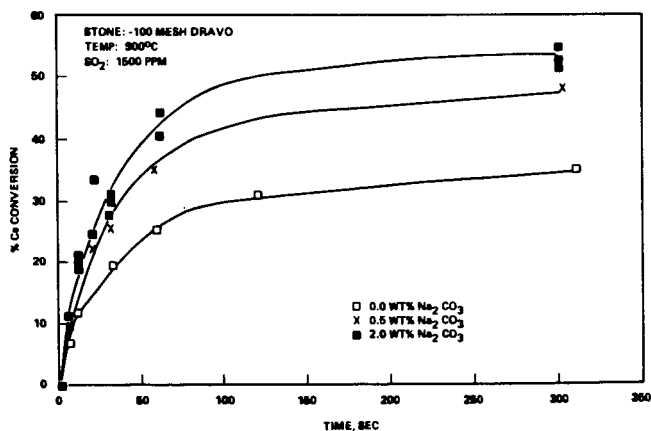

Figure 8. Sulfation Enhancement by Na$_2$CO$_3$ Additive.